PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Antiknock Compounds

We, ETHYL CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 100, Park Avenue, New York 17, State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved compositions for hydrocarbon fuels of the gasoline boiling range for use in spark ignition internal combustion engines.

Iron and nickel carbonyls are known as antiknock materials for internal combustion engine fuels. The disadvantages inherent in these carbonyls have prevented their commercial acceptance, and a great deal of effort has been expended in an endeavour to overcome these disadvantages.

According to the present invention the antiknock properties of hydrocarbon fuels are improved by providing a hydrocarbon fuel of the gasoline boiling range for use in spark ignition internal combustion engines containing from 0.1 to 6 grams of manganese, in the form of manganese pentacarbonyl, per gallon of fuel, this amount being sufficient to improve the antiknock properties of said hydrocarbon fuel.

The manganese carbonyl used as an antiknock agent according to this invention can be prepared by a number of methods among which is a recently disclosed process which comprises the reduction of manganese halides, for example, manganese iodide, with a reducing agent, one such material which is satisfactory being the alkyl magnesium halides in the presence of carbon monoxide at elevated temperature and pressure.

Manganese carbonyl is a solid at ordinary temperatures, having a melting point somewhat lower than 100° C. The proportions of the manganese to the carbonyl groups in the compound is such as to be adequately described by the empirical formula $[Mn(CO)_5]_2$. The formula is written in this fashion since theoretical considerations lead to the belief that manganese carbonyl exist as a dimer of manganese pentacarbonyl. The formula indicates that on an average there are about 5 carbonyl groups to 1 manganese atom. The density of manganese carbonyl is about 1.2 and the material possesses a vapor pressure of 1 millimeter of mercury at 50°. Manganese carbonyl is stable in the ordinary sense of the term up to a temperature of about 130° C. The solubility of manganese carbonyl is such as to make it ideally suited as a hydrocarbon fuel additive. It is soluble in most solvents possessing about the same solvency power as hydrocarbons, but is insoluble in water, aqueous solutions or certain polar solvents such as, for example, acetone.

The fuel with which the antiknock agent of this invention can be blended, may be any of the commercial hydrocarbon fuels of the gasoline boiling range. These fuels are usually blends of two or more components and can contain all types of hydrocarbons including paraffins both straight and branched-chain, olefins, cycloaliphatics containing paraffin or olefin side chains, and aromatics containing aliphatic side chains. The fuel type depends on base stock from which it is obtained and on the method of refining, for example, it can be a straight run or processed hydrocarbon, including thermally cracked, catalytically cracked, reformed, hydroformed, and so on. The boiling range of the components of the gasoline can vary from 0 to about 430° F.

although the boiling range of the fuel blend is often found to be between an initial boiling point of from about 80° F. to 100° F. and a final boiling point of about 430° F. While the above is true for ordinary gasoline, the boiling range is a little more restricted in the case of aviation gasoline. Specifications for the latter often require that the boiling range be from about 82° F. to about 338° F. with certain fractions of the fuel boiling away at a particular intermediate temperature.

The hydrocarbon fuels in which the antiknock agent of this invention can be employed, often contain minor quantities of various impurities. One such impurity is sulfur which can be present either in a combined form as an organic or inorganic compound, or as the elemental sulfur. The amounts of such sulfur can vary in various fuels from about .003 per cent to about .30 per cent by weight. Fuels containing quantities of sulfur both lesser and greater than the range of amounts referred to above, are also known.

The amount of manganese carbonyl used to provide a finished fuel of the desired octane number can be determined by one of the accepted octane rating methods, such as the Research or Motor Methods of the American Society for Testing Materials (ASTM) or various road rating methods. In general, however, we prefer to employ amounts not greatly exceeding about six grams of manganese per gallon of fuel. For most fuels for use in automotive engines the required amount will be substantially below the maximum, while for fuels for aircraft engines where the octane number requirement is considerably higher the amount of manganese employed may approach this maximum. Thus, the amount of manganese in the form of manganese carbonyl that can be added to a hydrocarbon fuel of the type described above is from about 0.01 grams to about 6 grams per gallon of the fuel. As will be shown in the examples given below, good results are obtained when the amount of manganese per gallon of fuel is within the range of from 0.2 grams to about 4 grams which constitutes a preferred embodiment of this invention. When the fuel is employed in an ordinary automobile engine, an especially preferred range of concentrations of manganese carbonyl in the fuel is from about 0.3 to about 3.0 grams of the metal per gallon of fuel.

In addition to the manganese carbonyl antiknock agent and sulfur impurities, other components may also be present in the hydrocarbon fuel. Such other components may be antioxidants, stabilizers, and dyes, specific examples of which are N,N'-disecondarybutyl-*p*-phenylene diamine and 2,4-dimethyl-6-tert-butylphenol.

One of the unexpected features of the additive of this invention is that it should turn out to be the most effective antiknock agent tested to date, when it is considered that manganese is located in the periodic table next to the element, chromium, the carbonyl of which exhibits pro-knock qualities when employed in a fuel in a spark ignition internal combustion engine as shown in Table I below.

An important advantage of the improved fuels of this invention is the very low wear-rate observed when manganese carbonyl is employed as an antiknock additive. The value of this feature wil be appreciated upon consideration of the effort expended in an attempt at a solution of the wear problem connected with the use of iron carbonyl, one of the most effective antiknock agents known prior to the present invention. The magnitude of the decrease in the amount of wear observed when fuel compositions of this invention are employed is shown in Table II, below.

An advantage that manganese carbonyl possesses as an antiknock agent over organolead compounds when employed in fuels for spark ignition internal combustion engines, is that oxides of manganese produced in the compositions of fuels containing manganese carbonyl have a higher melting point than oxides and salts of lead, and therefore, have less tendency towards fusing or sintering. Consequently, the build-up of a hard continuous deposit is prevented or greatly reduced. Any deposits which may be formed during the normal course of engine operation will flake or sluff off and be expelled from the combustion chamber.

One of the advantages not to be overlooked in providing the manganese carbonyl compound of the invention is the availability of the metal element which is an ingredient thereof. For example, manganese comprises approximately 0.096 per cent of the total elements in the earth's crust whereas lead, the most widely employed antiknock material to date, comprises the extremely low figure of 2×10^{-5} per cent of the earth's crust.

In order to illustrate some of the advantages of employing the manganese carbonyl antiknock agent of the invention, a number of tests have been run and the results thereof are contained hereinbelow. For example, to demonstrate the increase in octane rating provided to a low octane fuel, we determined, by the Research Method, the octane rating of a typical test fuel to which had been added in vary-

ing proportions manganese carbonyl, as well as other previously known carbonyl compounds. The Research Method of determining the octane number of a fuel is generally accepted as a method of test which gives a good indication of fuel behaviour in full-scale, automotive engines. The Research Method of testing antiknock is conducted in a single cylinder engine especially designed for this purpose and referred to as the CFR engine. This engine has a variable compression ratio and during the test the temperature of the jacket water is maintained at 212° F. and the inlet air temperature is controlled at 125° F. The engine is operated at a speed of 600 rpm with a spark advance of 13° before top dead center.

A typical method of providing fuels containing dissolved manganese is as follows. To a mixture corresponding to 60 parts by volume of isooctane and 40 parts by volume of *n*-heptane in a vessel provided with an agitator, we added manganese carbonyl in amount equivalent to 6.30 grams of manganese carbonyl per one gallon of the fuel blend. After agitating the mixture for approximately fifteen minutes the manganese carbonyl was completely dissolved and uniformly distributed throughout the fuel. This was demonstrated by analysis of a portion of the fuel for manganese, which showed the fuel to contain 1.77 grams of manganese per gallon of fuel mixture.

To demonstrate the remarkable effectiveness of manganese carbonyl as an antiknock additive, we employed a fuel as above comprising 60 per cent isooctane and 40 per cent *n*-heptane. Such a fuel has by definition an octane rating of 60. When sufficient manganese carbonyl was added to provide one gram of manganese per gallon of fuel, the octane number of the resulting fuel was 77.5, an increase of 17.5 octane numbers over the base fuel. When, on the other hand, iron carbonyl was added to this fuel in a quantity sufficient to provide one gram of iron per gallon of fuel the octane number of the resulting mixture was 74.5 as determined in the CFR engine. When sufficient tetraethyllead was added to this base fuel of 60 octane number to provide one gram of lead per gallon, the octane number of the resulting fuel mixture was 71.5. Therefore, the increase when manganese carbonyl is used is 6.0 octane numbers over tetraethyllead and 3.0 octane numbers over iron carbonyl, at equivalent amounts on a metal weight basis.

In order to provide the same octane rating to the above fuel by the use of the prior antiknocks, sufficient tetraethyllead and iron carbonyl was required to provide 1.6 and 1.25 grams of lead and iron, respectively, per gallon of fuel. Thus, at an octane number increase of 17.5, the manganese used according to the invention is 160 and 125 per cent as effective respectively as lead and iron, on a metal weight basis.

When the amount of manganese carbonyl was increased so as to provide a fuel containing 1.77 grams of manganese per gallon of uel, the resulting octane number of the fuel was 84.3. The same fuel, with sufficient additive to provide 1.77 grams of lead or iron per gallon of fuel, has an octane number of 78.7 and 82.0 respectively. An increase of 5.6 octane numbers was therefore obtained employing manganese carbonyl over tetraethyllead and 2.3 octane numbers over iron carbonyl on an equal metal weight basis.

In order to provide an 84.3 octane number fuel from a 60-octane mixture of 60 per cent isooctane and 40 per cent *n*-heptane using tetraethyllead or iron carbonyl as the antiknock additive, it is necessary to employ enough tetraethyllead or iron carbonyl to provide 3.33 grams of lead or 2.1 grams of iron per gallon of fuel, respectively. Comparing this with the 1.77 grams of manganese as manganese carbonyl, it is seen that by the Research Method manganese carbonyl at this concentration is 188 per cent as effective on a metal weight basis as tetraethyllead and 120 per cent as effective as iron carbonyl.

To further illustrate the unexpected property of manganese carbonyl as an antiknock agent compared to the carbonyl of its neighbor in the Periodic Table, and with the carbonyl of tungsten, tests similar to the ones described above were run using chromium carbonyl and tungsten carbonyl as the additives. The chromium carbonyl was run in a fuel composition similar to the one described above, namely, 60 per cent isooctane and 40 per cent *n*-heptane and denoted as Fuel " A " in Table I, while tungsten was run in a fuel containing 70 per cent isooctane and 30 per cent *n*-heptane. The latter by definition has a relative octane number of 70, and is indicated as Fuel " B " in the table. The results of these tests are contained in Table I shown below:—

TABLE I

Fuel	Additive	Concentration of additive in grams/gallon	Concentration of the metal in grams/gallon	Relative octane number
A	——	0	0	60.0
A	$Cr(CO)_6$	(approx. 1.7)	(approx. 0.40)	54.3
A	$Cr(CO)_6$	saturated soln. (approx. 3.0)	saturated soln. (approx. 0.71)	53.7
B	——	0	0	70.0
B	$W(CO)_6$	4.63	2.42	65.2
B	$W(CO)_6$	9.25	4.83	59.4
B	$W(CO)_6$	18.5	9.66	60.6

The experiments described hereinabove present a view of the antiknock effectiveness of a representative number of carbonyl compounds and illustrate the unexpected superiority of manganese carbonyl in this respect. The antiknock properties of the manganese carbonyl are even more unexpected when it is considered that some other compounds of manganese are ineffective. For example, manganese naphthanate exhibits a slight pro-knock quality.

To demonstrate the low wear rate caused by the use of manganese carbonyl as an antiknock agent in fuel as compared to the wear caused when iron carbonyl is employed for the same purpose, tests were conducted in which a fuel consisting of technical isooctane, containing manganese carbonyl on the one hand and iron carbonyl on the other, was employed in a single cylinder engine having a displacement of 35 cubic inches operating at a speed of 1850 rpm, at a jacket temperature of 180° F. The intake air was filtered in order to prevent dust in the atmosphere from entering the combustion chamber. The amount of wear was determined according to the method disclosed in U.S. Patent 2,315,845. The method covered by this patent involves determining wear, particularly of piston rings, by incorporating a radioactive substance in a surface normally subjected to abrasive wear, causing this surface to be abraided in the presence of a liquid (lubricating oil) capable of receiving the abraided particles and then determining the radioactivity of the liquid. It is reported in Table II below as the rate of loss in weight of the upper piston ring during the test period, in terms of milligrams per hour. The piston ring in question was made of standard cast iron and contained radioactive isotopes. As the surface of this ring was subjected to wear in the operation of the engine on a particular fuel, the wear debris was carried into the lubricating oil where its concentration was measured by determining the radioactivity of the oil solution by means of a counting device. The radioactivity count was then compared with the count obtained from a standard solution of metal secured from the surface of a piston ring similar to the one used in the test. By appropriate mathematical calculations, the observed count of radioactivity of the oil was transformed to figures representing the loss in weight of the piston ring due to wear in the operation of the engine.

TABLE II

COMPARISON OF TOP PISTON RING WEAR IN A SINGLE CYLINDER TEST ENGINE USING TECHNICAL ISOOCTANE AS THE FUEL

Additive	Additive conc. in g. of metal/gal.	Sulfur content weight %	Fuel/air ratio	Duration of test hours	Wear rate mg./hr.
Part I					
$Fe(CO)_5$	0.21	——	0.080	23	0.646
$Fe(CO)_5$	0.21	——	0.065	19.5	0.770
$Fe(CO)_5$	0.21	0.15	0.080	20	0.86
$Fe(CO)_5$	0.21	0.15	0.080	23	1.02
			Average		0.824
Part II					
$Mn(CO)_5$	0.21	——	0.065	18	0.241
$Mn(CO)_5$	0.21	——	0.065	20.25	0.155
			Average		0.198
Part III					
$Fe(CO)_5$	0.62	——	0.080	22.5	2.36
$Fe(CO)_5$	0.62	——	0.080	20	4.52
			Average		3.44
Part IV					
$Mn(CO)_5$	0.62	——	0.065	15	0.535

It is seen from Table II that at a concentration of the carbonyl compound equivalent to 0.21 grams of the metal per gallon of fuel, manganese carbonyl produces only 24 per cent of the wear observed when iron carbonyl is used as the additive. It is further seen that when the concentration of the additive is increased to that equivalent to 0.62 grams of the metal per gallon of fuel, the amount of wear due to the use of manganese carbonyl is only 15.5 per cent of that observed when iron carbonyl is the additive. Stating this in a different manner, iron carbonyl has been shown, as indicated in the above table, to produce from 416 per cent to 645 per cent as much wear as manganese carbonyl produced in the combustion chamber of the spark fired internal combustion engine when used as an antiknock additive in fuel. This further illustrates the desirability of employing manganese carbonyl as an antiknock additive in fuel compositions.

Another manganese compound that can be used as an antiknock agent is manganese carbonyl hydride. When this compound is blended with hydrocarbon fuels and tested for antiknock quality and wear-causing characteristics, very good results are obtained.

What we claim is:—

1. A hydrocarbon fuel of the gasoline boiling range for use in spark ignition internal combustion engines containing from 0.01 grams to 6 grams of manganese, in the form of manganese pentacarbonyl, per gallon of the fuel, this amount being sufficient to improve the antiknock properties of said hydrocarbon fuel.

2. A hydrocarbon fuel according to Claim 1, containing from 0.2 grams to 4.0 grams of manganese in the form of manganese pentacarbonyl, per gallon of fuel.

3. A hydrocarbon fuel of the gasoline boiling range for use in spark ignition internal combustion engines substantially as herein described.

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